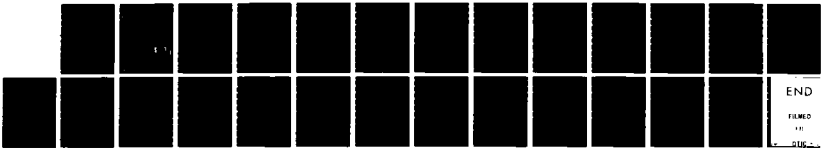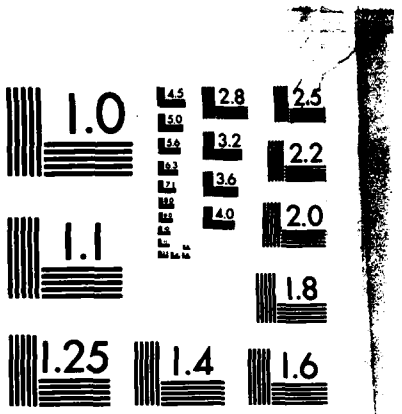
AD-A131 863 THERMOLYSIS OF 4-METHYL-4-PHENYL MALONYL PEROXIDE: A NEW OXYGEN DEPENDENT.. (U) ILLINOIS UNIV AT URBANA ROGER ADAMS LAB J E PORTER ET AL. 08 AUG 83 N00014-76-C-0745 1/1

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER N0014-76-C-0745/34	2. GOVT ACCESSION NO. AD-A131 863	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) "Thermolysis of 4-Methyl-4-phenyl Malonyl Peroxide: A New Oxygen Dependent Chemiluminescent Reaction"		5. TYPE OF REPORT & PERIOD COVERED Technical 6. PERFORMING ORG. REPORT NUMBER
AUTHOR(s) Judith E. Porter and Gary B. Schuster		8. CONTRACT OR GRANT NUMBER(s) N0014-76-0745
PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Illinois Urbana, IL 61801		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-051-616
CONTROLLING OFFICE NAME AND ADDRESS Chemistry Program, Materials Science Division, Office of Naval Research, 800 N. Quincy St., Arlington, Virginia 22217		12. REPORT DATE August 8, 1983 13. NUMBER OF PAGES 25
MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

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18. SUPPLEMENTARY NOTES

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
chemiluminescence
cyclic peroxides
CIEEL

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Thermolysis of 4-methyl-4-phenyl malonyl peroxide in acetonitrile is accelerated by electron donors, such as perylene. When both the perylene and oxygen are present in solution the reaction gives acetophenone and a small amount of light. Investigation of the mechanism of light generation reveals that it involves formation and fragmentation of a tetraoxide. The chemically initiated electron-exchange luminescence mechanism (CIEEL) appears to be responsible for light generation.

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Contract N0014-76-C-0745

Task No. NR-051-616

TECHNICAL REPORT NO. N0014-76-C-0745-34

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by

Judith E. Porter and Gary B. Schuster

Prepared for Publication

in

Journal of Organic Chemistry

School of Chemical Sciences

University of Illinois

Urbana, Illinois 61801

August 8, 1983

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Thermolysis of 4-Methyl-4-phenyl Malonyl Peroxide: A New Oxygen Dependent Chemiluminescent Reaction.

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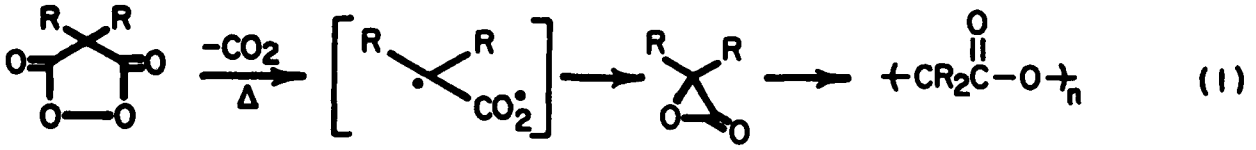
Urbana, IL 61801

Abstract. Thermolysis of 4-methyl-4-phenyl malonyl peroxide in acetonitrile is accelerated by electron donors, such as perylene. When both the perylene and oxygen are present in solution the reaction gives acetophenone and a small amount of light. Investigation of the mechanism of light generation reveals that it involves formation and fragmentation of a tetraoxide. The chemically initiated electron-exchange luminescence mechanism (CIEEL) appears to be responsible for light generation.

Extensive research over the past 50 years has revealed that nearly all of the known chemiluminescent reactions of organic compounds in solution involve the conversion of a peroxide linkage to a carbonyl group.[1] The molecular basis of this selectivity is tied strongly to the energy required to generate light. Only reactions capable of releasing at least 40 kcal/mol of energy can generate visible light, and few reactions other than peroxide fragmentations can satisfy this requirement.

Complementing the requirement of energy sufficiency is a mechanistic requirement for chemiluminescence. There must be a path that directs the potential energy stored in the peroxide toward formation of an electronically excited state of a product. Two such paths have been found to operate.[1] The first is a unimolecular reaction of a peroxide, typically proceeding through a biradical, to generate directly an excited product. The second is the sequence of reactions we have identified as chemically initiated electron-exchange luminescence (CIEEL).[2]

For reasons we have detailed previously,[3] malonyl peroxides possess several characteristics that may make them efficient sources of chemiluminescence by the CIEEL path. The thermal and photochemical properties of malonyl peroxides were first investigated by Adam and his coworkers[4] who found that simple alkyl substituted examples decarboxylate and then cyclize to α-lactones. The lactones typically are not isolable, but go on to form polyester. This sequence of reactions is illustrated in eq. 1.



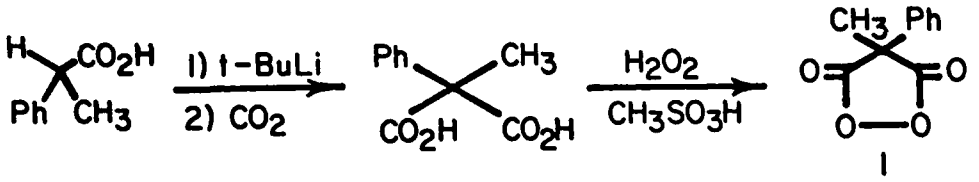
(1)

In order for malonyl peroxides to generate light efficiently by the CIEEL path their reaction must be catalyzed by electron donation from an activator (ACT). Also, to satisfy the energy requirement, the biradical shown in eq. 1 must be diverted away from formation of α-lactone toward a more exothermic path. Our recently reported study of the thermal chemistry of cyclopropyl-substituted malonyl peroxides showed that the first requirement is easily met. However, the cyclization of the biradical to the α-lactone is apparently faster than even the rearrangement of the cyclopropylcarbinyl radical to the allylcarbinyl radical.[5] Thus, easily detected but very inefficient chemiluminescence is observed from these specially constructed peroxides.[3]

Reasoning that resonance stabilization of the biradical shown in eq. 1 would slow the formation of α-lactone and permit other reactions to compete successfully, we prepared and investigated the thermal and chemiluminescent properties of 4-methyl-4-phenyl malonyl peroxide (1). This peroxide does undergo unusual reactions that are described herein.

Results and Discussion

2-Methyl-2-phenylmalonic acid is prepared conveniently, and in good yield, from the reaction of 2-phenylpropionic acid first with two equivalents of t-butyl lithium, and then with CO_2. The diacid is converted to peroxide 1 in 40% yield by reaction with hydrogen peroxide in methanesulfonic acid according to the procedure described by Adam and Rucktäschel.[4a] These transformations are outlined in eq. 2, and the details are presented in the Experimental section.

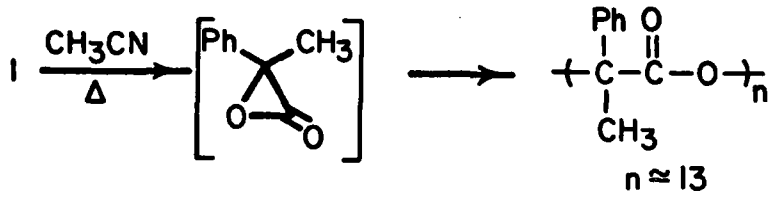


(2)

1

Malonyl peroxide 1 is a low melting solid that is stable indefinitely at 0°C. The energy content of this compound is quite high and, therefore, it should be treated cautiously. However, despite several attempts, we have been unable to initiate a violent reaction of 1.

Unlike many of the other malonyl peroxides that have been investigated, the reaction path followed by peroxide 1 depends markedly on the reaction conditions. Thermolysis in deoxygenated acetonitrile produces nearly a quantitative yield of polyester. We presume that this arises from reaction of the undetected α-lactone, eq. 3. Similarly, thermolysis of 1 in air, or



(3)

oxygen saturated acetonitrile gives only polyester. Also, when the reaction of 1 is catalyzed by perylene in the absence of oxygen (vide infra) polymer is the only observed product, and no chemiluminescence is detected. However, when the thermal reaction of malonyl peroxide 1 is carried out with both oxygen and perylene present, acetophenone is formed as a major product and weak, but easily detected, chemiluminescence is observed. The perylene is a true catalyst

in this reaction and is not consumed. The chemiluminescence emission spectrum corresponds exactly to the fluorescence spectrum of the perylene. These findings are summarized in eq. 4.

$$\text{I} + O_2 + \text{Perylene} \xrightarrow[\Delta]{CH_3CN} \text{Ph}\overset{O}{\overset{\|}{C}}\text{CH}_3 + (\text{Perylene})^{*1} \longrightarrow \text{Perylene} + \text{Light} \qquad (4)$$

The yield of acetophenone and light both depend directly on the partial pressure of oxygen above the reaction solution at pressures below 0.5 atm. This is shown on Figure 1 where the yield of acetophenone is seen to reach a maximum at ca. 42%. These findings suggest that an intermediate that reacts with oxygen to form eventually acetophenone and light is generated in the presence of perylene, but not in its absence. To confirm this possibility we undertook the isotopic tracer and kinetic study of this reaction.

To illuminate the role of oxygen in the formation of acetophenone, the perylene catalyzed reaction of I was carried out in the presence of O_2^{36}. Mass spectroscopic analysis of the acetophenone shows that more than 85% of the ketone has incorporated an O^{18}. Thus, in contrast to previous suggestions that formation of ketones in the thermolysis of malonyl peroxides comes from decarbonylation of the intermediate α-lactone,[4] our findings indicate that for I nearly all of the ketone formed is a consequence of reaction with oxygen. Furthermore, analysis by FT-IR spectroscopy of the gasses formed during the reaction shows no detectable (<2%) carbon monoxide. This result has further significance in the consideration of the reaction mechanism.

The role of perylene, and the origin of the chemiluminescence was probed by studying the reaction kinetics. In other examples of CIEEL from

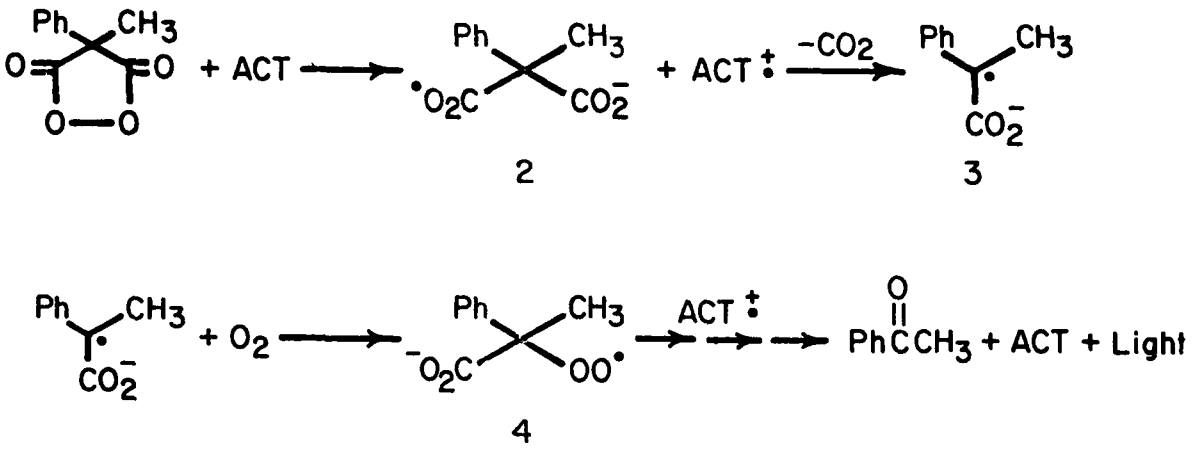
malonyl peroxides, and other systems,[1,2] it is found that the observed pseudo first-order rate constant for reaction (k_{obs}) is composed of two parts. The first is a unimolecular rate constant (k_1) characteristic of thermolysis of the peroxide. The second is a bimolecular rate constant (k_{cat}) whose magnitude depends on the nature of the peroxide and the oxidation potential of the ACT (in this case perylene), eq. 5

$$k_{obs} = k_1 + k_{cat}\,[ACT] \tag{5}$$

The rate of reaction of peroxide 1 catalyzed by perylene in air-saturated acetonitrile was determined by monitoring either the chemiluminescence emission intensity or the peroxide concentration, as indicated by its characteristic infrared absorption at 1804 cm^{-1}, as a function of time. Both techniques give the same result, which shows that the observed chemiluminescence is a consequence of the reaction of the peroxide. The data are plotted according to eq. 5 on Figure 2, and give $k_{cat} = 2.6 \pm .4\ s^{-1}\ \underline{M}^{-1}$ and $k_1 = 9.6 \pm 1.5 \times 10^{-5}\ s^{-1}$ at 70°C. Similar results are obtained with 9,10-diphenylanthracene (DPA) and 9,10-diphenylethynylanthracene (DPEA). But, 9,10-dibromoanthracene (DBA) gives virtually no light. This observation rules out direct formation of excited acetophenone as the light generating path.[6] Rubrene and ACT containing nitrogen are consumed by reaction with peroxide 1.

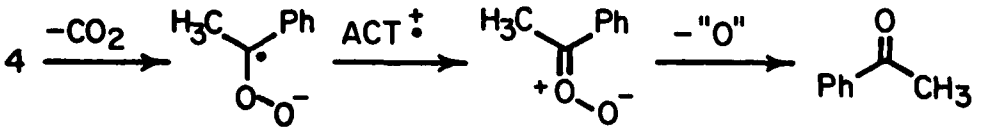
These observations suggest that the reaction sequence followed by 1 is the CIEEL path, and that the activators are acting as electron donors. In this circumstance it is reasonable that the intermediate trapped by oxygen is the radical anion corresponding to the suspected biradical of eq. 1. This partial mechanism is outlined in Scheme 1.

Scheme I

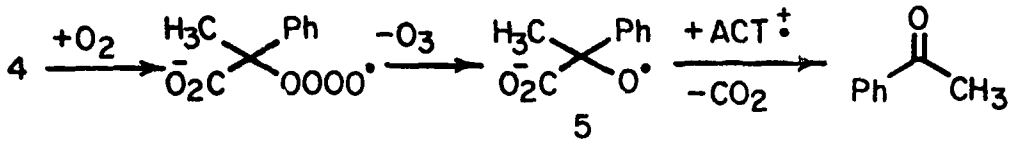


The initial interaction between the peroxide and the activator leads eventually to electron transfer and oxygen-oxygen bond cleavage to give radical anion 2 and activator radical cation ($ACT^{+\cdot}$). It is anticipated[7] that 2 will very rapidly lose CO_2 and form radical anion 3, which can transfer an electron back to the radical cation of the activator and form α-lactone, or 3 can be trapped by oxygen to give peroxy radical anion 4. Eventually 4 must lose CO_2, an oxygen atom, and an electron if it is to be transformed to acetophenone. Also, 4 is likely to be an intermediate on the path leading to light since the light yield parallels the acetophenone yield. We have carried out experiments that confirm the intermediacy of 4, or a related species, in the formation of acetophenone.

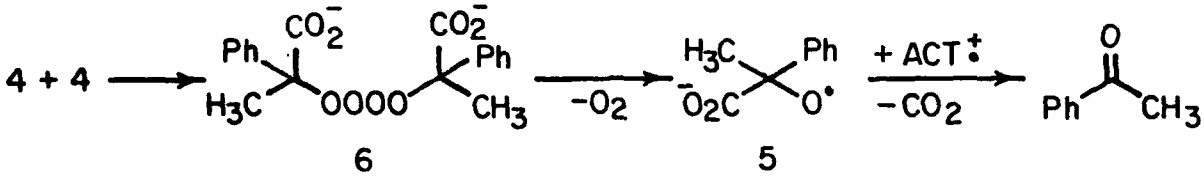
There are several reaction sequences that can convert 4 to acetophenone. Some possibilities are outlined in eqs. 6-8.



(6)



(7)



(8)

The initial decarboxylation suggested in eq. 6 generates a carbonyl oxide radical anion which, on reaction with activator radical cation, give acetophenone carbonyl oxide. To test this possibility we carried out the catalyzed reaction of 1 in the presence of styrene or cyclopentanone. These reagents are known to be good oxygen atom acceptors,[8,9] and their oxidation would suggest the intermediacy of a species, such as the carbonyl oxide, capable of transferring a single oxygen atom. However, no detectable oxidation of either of these reagents is found. And thus the sequence of eq. 6 is eliminated.

The sequence outlined in eq. 7 involves first trapping of 4 by oxygen to form a tetraoxide radical anion, and then the loss of ozone to give radical anion 5, which in turn neutralizes $ACT^{+\cdot}$ and loses CO_2. Simple bond energy calculations indicate that the conversion of 4 and O_2 to 5 and O_3 is mildly endothermic. Nevertheless, we attempted to detect ozone in the reaction mixture by sweeping the gasses formed by the reaction into a styrene solution and analyzing this solution for benzaldehyde, the known ozonolysis product.[10] None is found, and for this reason the sequence of eq. 7 is eliminated.

The dimerization of radical anion 4 to tetraoxide 6, as illustrated in eq. 8, has considerable precedence in the autooxidation of hydrocarbons.[11]

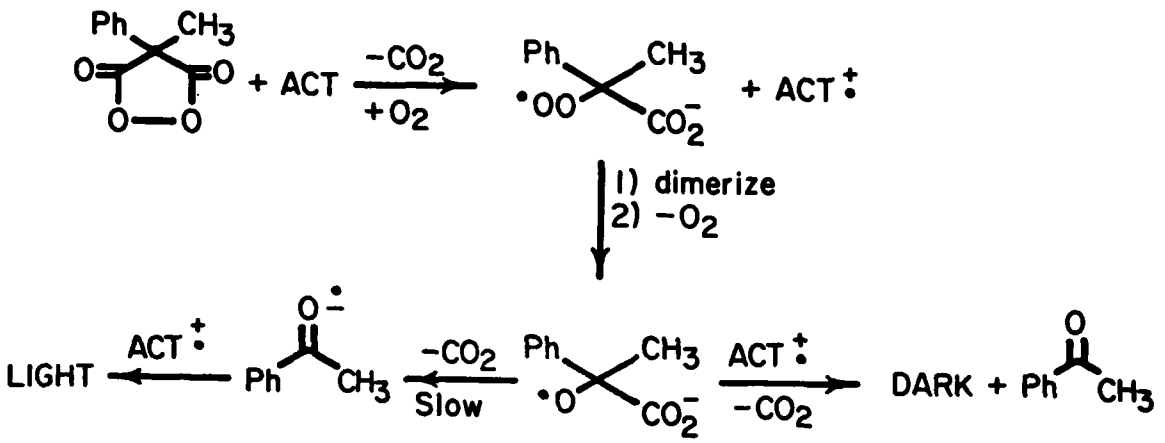
The intermediacy of a tetraoxide in that case was proved by an isotope exchange reaction. We have carried out a similar experiment on the perylene catalyzed reaction of malonyl peroxide 1.

Thermolysis of an acetonitrile solution of 1 containing perylene under an atmosphere consisting of ca. 50% O_2^{36} and 50% O_2^{32} gives the anticipated amount of O_2^{34} based on the observed yield of acetophenone. This result confirms both the formation of 4 (or a related species) as shown in Scheme 1, and its dimerization as outlined in eq. 8.

The rate of decay of the chemiluminescence is quite cleanly first-order, and the total chemiluminescence intensity is directly and linearly dependent on the concentration of peroxide 1. To maintain consistency with the oxygen isotope exchange experiment, these results require that dimerization of 4 be essentially its only fate.

The final steps in the reaction sequence require decarboxylation of 5 and back electron transfer to $ACT^{+\cdot}$. The experimental results require that some intermediate, formed after the reaction is committed to give acetophenone, is responsible for light generation. Although we have no direct evidence on this point, we suspect that decarboxylation of 5 to acetophenone radical anion before the annihilation with $ACT^{+\cdot}$ leads to electronically excited activator and thus light. On the other hand, reaction of radical anion 5 with $ACT^{+\cdot}$ before decarboxylation, perhaps by an addition-elimination sequence, gives only ground state products. In this model, the low yield of light is a consequence of the slow decarboxylation of 5. This mechanism for the chemiluminescence of 1 is summarized in Scheme 2.

Scheme 2



Conclusion

The properties of malonyl peroxide 1 reveal some interesting features of the thermal and electron transfer catalyzed reactions of these systems. Evidently, conjugation with a phenyl group does not slow the cyclization of the biradical in eq. 1 enough to permit its trapping by oxygen. However, the corresponding radical anion can be trapped by oxygen before back electron transfer to $ACT^{+\cdot}$ and cyclization to α-lactone. Thus, in this regard, we have accomplished our initial objective of diverting the malonyl peroxide away from α-lactone toward a more exothermic route. However, the yield of light from this system is still quite low, probably less than 0.1%. We presume that this is a consequence of slow loss of the second CO_2 to generate acetophenone radical anion. We are currently exploring ways to speed up this reaction to test this hypothesis.

Experimental:

General. Proton magnetic resonance spectra were recorded on a Varian Associates EM-390 using tetramethylsilane as the internal reference. IR spectra were recorded on a Nicolet 7199 FT-IR. Gas chromatographic analyses were done on a Hewlett Packard 5790A or a Varian 3700 gas chromatograph both equipped with a flame ionization detector. A 3 1/2 foot glass column packed with OV-101 (10%) on Chromosorb WHP (100/120 mesh) was used in all cases unless otherwise noted. GC/MS data were recorded on a Varian 311A mass spectrometer interfaced to a Varian 2700 gas chromatograph. Oxygen isotope gas analyses were recorded on a Nuclide Model 3-60-RMS mass spectrometer. Elemental analysis, active oxygen, and molecular weight determinations were performed by the Analysis Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois. Melting points were obtained with a Büchi Schmelzpunktbeststimmingapparat and are uncorrected.

Chemiluminescence measurements were performed as described previously.[12] The rate of reaction of peroxide 1 was determined by monitoring the decay of chemiluminescence. In a typical experiment, a 1 mL CH_3CN solution of 1 and activator was placed in a Pyrex cell equipped with a Teflon stopcock. The cell was placed in an electrically heated cell holder. After thermal equilibration to 70 °C (4-6 min) the chemiluminescence decay was monitored at the fluorescence maximum of the activator. The rate constant was determined by a least squares analysis of the intensity data.

Analysis of the reaction kinetics by FT-IR spectroscopy provided the rate of the thermolysis of peroxide 1 for both the catalyzed and uncatalyzed decompositions. Strict adherence to Beer's Law was established for the carbonyl absorption band (1804 cm^{-1}) of the peroxide. This absorption was then monitored as the reaction progressed. The acetonitrile used was obtained from Burdick and Jackson Inc. (Gold label) and distilled from CaH_2 before use.

2-Methyl-2-phenyl malonic acid. 2-Phenylpropionic acid (5.0 g, 0.033 mol, Aldrich) was dissolved in 200 mL dry THF (Na, benzophenone) and the solution cooled to -78 °C (under a N_2 atmosphere). A pentane solution of t-butyl lithium (35 mL, 2.3 M) was added dropwise to the cold solution which was then stirred at 0°C for one hour. Dry CO_2 was bubbled through the mixture for 45 min. The resulting off-white suspension was diluted with 350 ml of water, washed with ether, acidified to pH 5 with 10% aq. HCl, and extracted with 3 x 50 mL portions of ether. The organic layers were combined, dried with $MgSO_4$, filtered, the solvent evaporated, and the resulting white solid recrystallized from 3:1 ethyl ether/$CHCl_3$ to give 3.9 g (0.020 mol, 79%) of the acid, mp 158-159 °C; NMR (acetone-d_6) δ 7.2-7.6 (m, 5 H), δ 1.85 (s, 3 H); IR (CH_2Cl_2) $\gamma_{C=O}$ 1732 cm^{-1}.

Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.86; H, 5.15. Found: C, 61.97; H, 5.18.

4-Methyl-4-phenyl-1,2-dioxolane-3,5-dione. 2-Methyl-2-phenyl malonic acid (0.50 g, 2.6 mmol) was added to 5 mL of ether at 0 °C and 1 mL of CH_3SO_3H was added to the resulting solution. Hydrogen peroxide (90%, 1 mL, 3.8 mmol) was added dropwise to the cooled solution at a rate that kept the temperature < 10 °C. The solution was warmed to room temperature and then stirred for 17 h and poured over ice (25 g). The reaction mixture was diluted with 50 mL saturated $(NH_4)_2SO_4$, extracted with 3 x 20 mL of pentane, and the combined organic layers dried with $MgSO_4$. The residue after removal of the solvent was recrystallized from cold pentane to give 0.20 g (1.0 mmol, 40%) white crystals, mp 34-35 °C; NMR ($CDCl_3$) δ 7.45 (s, 5 H), δ 1.9 (s, 3 H); IR (Et_2O) $\gamma_{C=O}$ 1804 cm^{-1}.

Anal. Calcd for $C_{10}H_8O_4$: C, 62.50; H, 4.17; active oxygen, 8.33; molecular weight, 192. Found: C, 62.57; H, 4.25; active oxygen, 8.07; molecular weight (osmometry), 200.

Thermolysis of peroxide 1 in CH_3CN. Peroxide 1 (0.40 g, 2.1 mmol) was added to 25 mL dry CH_3CN and the solution was heated at reflux for 18 h. The CH_3CN was removed under vacuum and the residue was reprecipitated from pentane to give an off-white solid (0.38 g; 95%, based on 1); NMR ($CDCl_3$) δ 7.45 (broad s), δ 1.9 (broad s); IR ($CDCl_3$) $\nu_{C=O}$ 1756 cm^{-1}.

Anal. Calcd for $(C_9H_8O_2)_n$: C, 72.20; H, 5.41. Found: C, 72.97; H, 5.67; molecular weight (osmometry), 1930.

Thermolysis of peroxide 1 in presence of O_2[36]. An CH_3CN solution of peroxide 1 (1 mL, 5×10^{-3} M) and perylene (1 mL, 5×10^{-3} M) was placed in a glass tube, frozen and evacuated. 760 torr of O_2[36] were placed over the solution and the tube sealed. The solution was thermolyzed at 70 °C for 1 h. Mass spectral analysis of the acetophenone gave a ratio of 1:5.5 for the m/e 120 to 122 peaks, which indicates $\sim$ 85% incorporation of oxygen-18.

Attempted trap of carbonyl oxide. An air-saturated CH_3CN solution of 1 (0.25 mL, 2×10^{-2} M), perylene (0.25 mL, 2×10^{-2} M), and a 10-fold excess of styrene or cyclopentanone (0.25 mL, 2×10^{-1} M) was thermolyzed at 70 °C. The chemiluminescence intensity was monitored to show that the trapping reagent does not react directly with the peroxide. The thermolyzed solutions were analyzed by gas chromatography (3 ft, 15% carbowax on ChromWHP, 100 °C, 34 ml/min) for δ-valerolactone in the case of cyclopentanone and for styrene oxide in the styrene solutions. Neither was observed, and control experiments revealed that ca. 2% of these oxidation products (based on the amount of peroxide 1) could be detected.

Ozone trapping experiment. An CH_3CN solution of peroxide 1 (10 mL, 5×10^{-2} M) and perylene (4×10^{-2} M) was thermolyzed at 70 °C in a round-bottom flask while being bubbled vigorously with a steam of dry air. The effluent gases were passed through a CH_2Cl_2 solution of styrene at 0 °C (10 mL, 7×10^{-2} M). This solution was treated with 1 mL MeOH and 3 drops of dimethylsulfide. The resulting solution was analyzed by gas chromatography (3 ft, 10% OV-101 on ChromWHP, 95 °C, 30 ml/min) for benzaldehyde. None was detected. A control experiment where a CH_2Cl_2 solution of styrene (25 mL, 5×10^{-2} M) was bubbled with O_3 (1.5 mmol/min for 0.33 min) revealed that ca. 2-3% yield of benzaldehyde (based on the amount of peroxide 1) could be detected.

Thermolysis of peroxide 1 in mixed oxygen atmosphere. An CH_3CN solution of peroxide 1 (1 mL, 8×10^{-2} M) and perylene (1 mL, 2×10^{-3} M) in a glass tube was frozen at -78 °C, evacuated to 0.1 mm, and charged with equal amounts of O_2^{32} and O_2^{36} gas to a total pressure of 111 mm. The tube was sealed and then thermolyzed at 70 °C. The gases above the sample were analyzed by mass spectrometry which revealed the oxygen isotope ratios shown in Table I.

Acknowledgment. We thank Dr. John Hurst of this department for the use of his computer programs and Dr. Richard Mulvaney of the Department of Agronomy, University of Illinois, for his assistance in the oxygen isotope ratio analyses. This work was supported by the Office of Naval Research.

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Table I. Oxygen Isotope Ratios from Mixed O_2 Atmosphere Thermolysis of 1

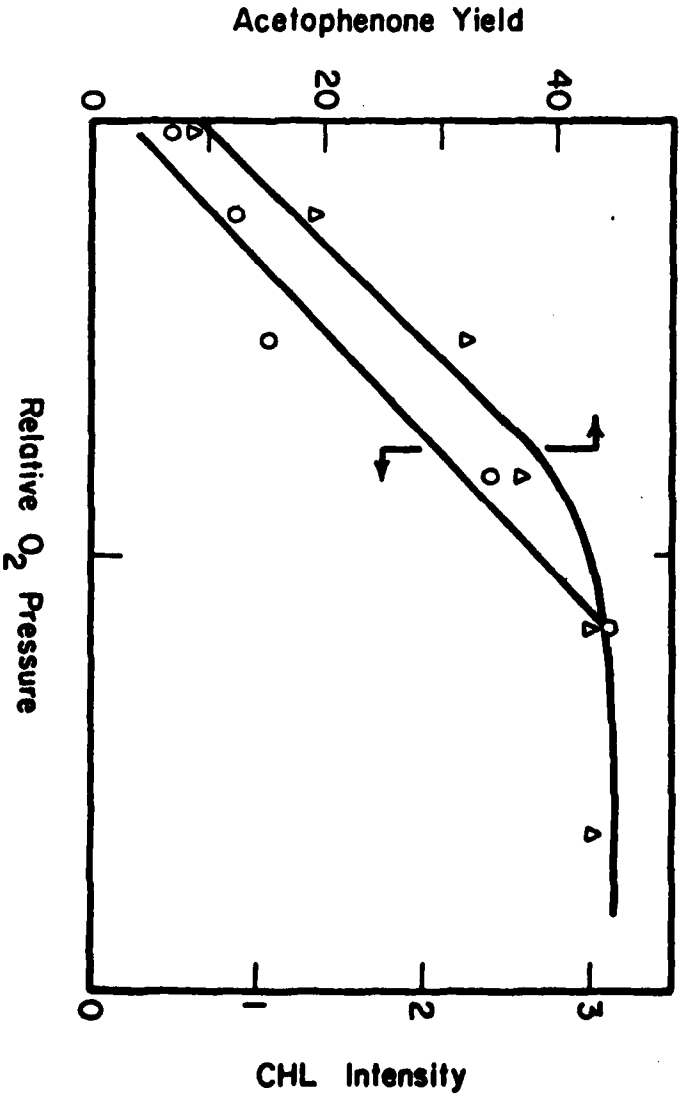
	O_2^{32}	O_2^{34}	O_2^{36}
Start[a]	1.0	0.05	1.0
Expected Final[b]	1.0	0.11	1.0
Actual Final[a]	1.0	0.10	1.0

[a]By mass spectrometry. [b]Assuming a statistical consumption of a 1:1 ratio of O_2^{32}/O_2^{36} and production of a 1:2:1 ratio of $O_2^{32}/O_2^{34}/O_2^{36}$.

Captions for Figures

Figure 1. Effect of increasing oxygen pressure on the yield of acetophenone (triangles, lefthand axis) and on the relative chemiluminescence yield (circles, righthand axis).

Figure 2. Effect of increasing perylene concentration on the observed first-order rate constant for reaction of peroxide 1 in CH_3CN.


Acetophenone Yield
0
20
40
Relative O_2 Pressure
0
1
2
3
CHL Intensity

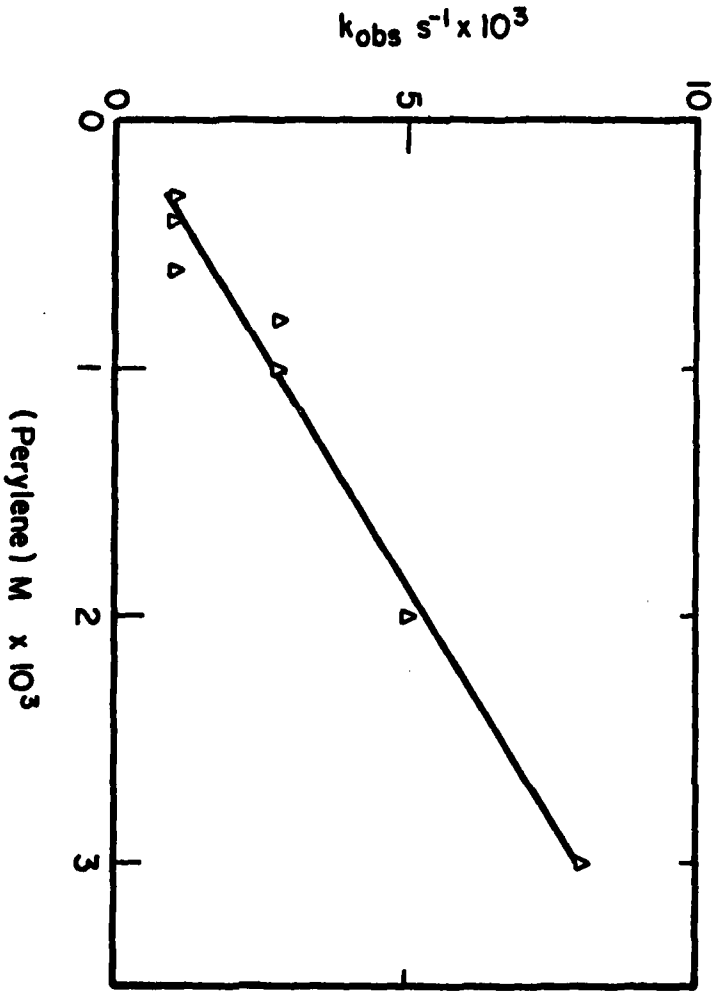


Figure 2.

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